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PB-261 914

Equilibrium Partial Pressure of Sulfur Dioxide in Alkaline Scrubbing Processes

Environmental Protection Agency, Research Triangle Park, N C

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Oct 76

012032

PB 261 914

EPA-600/2-76-279
October 1976

Environmental Protection Technology Series

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EPA-600/2-76-279
October 1976

EQUILIBRIUM PARTIAL PRESSURE OF SULFUR DIOXIDE IN ALKALINE SCRUBBING PROCESSES

by

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ROAP No. 21ADE
Program Element No. 1AB013

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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ACKNOWLEDGMENTS

The help of the technicians who made many of the measurements contributing to this report is gratefully acknowledged. The technicians most directly involved in this work were Messrs. Don Mitchell and Ron Collier. The help of Mrs. Ellen White and Mr. Frank Briden was also very valuable in the areas of data analysis and computer programming. Lastly, the typing skills of Mrs. Brenda Foil are gratefully acknowledged.

INTRODUCTION

A number of alkaline scrubbing processes are being developed for SO_2 control in which the sorbent is regenerated. A notable example of this is the Wellman-Lord Process[1]. Among other systems proposed is the U. S. Bureau of Mines Citrate Process[2] in which the regeneration is accomplished by an aqueous Claus or Wackenroder reaction and elemental sulfur is the product.

The maximum removal efficiency at any point in the scrubbing cycle of any of these processes is related to the equilibrium partial pressure of SO_2 above the solution. Thus, if the equilibrium partial pressure of SO_2 above the scrubbing liquor is equal to the partial pressure of SO_2 in the incoming gas stream, there will be no removal.

Conversely, during the stripping cycle, steam requirements increase as the cycle progresses and the equilibrium partial pressure of SO_2 decreases for the scrubber liquor. Consequently, a knowledge of equilibrium P_{SO_2} is required to operate the stripping cycle economically.

Historically, theoretical equations developed by Dr. H. F. Johnstone[3] in 1935 have been used to calculate equilibrium partial pressures for scrubber design. The equation given by Johnstone is:

$$P_{SO_2} = M \frac{(2S - C)^2}{C - S} \qquad \text{(equation 1)}$$

where P_{SO_2} = equilibrium partial pressure of SO_2, mm Hg

S = total concentration of dissolved S^{+4}/100 moles H_2O

C = Total concentration of the cation associated with the S^{+4}/100 moles H_2O

M = a constant depending on T (^oK) and the type of scrubbing system (for the $Na_2SO_3/NaHSO_3$ system, $\log M = 4.619 - 1987/T$)

Equation (1) considers only the equilibrium which exists between sulfite and bisulfite ions and ignores the other important equilibria which exist in this extremely complex system. Within the framework given by equation (1), and considering the $KHSO_3$/ K_2SO_3 system, by definition the ratio S/C goes from 0.5 for a completely stripped solution of K_2SO_3 to 1.0 for a completely saturated solution of $KHSO_3$. The reaction during the scrubbing cycle is thought to be:

$$SO_3^{=} + SO_2 + H_2O \underset{\text{stripping}}{\overset{\text{scrubbing}}{\rightleftharpoons}} 2HSO_3^- \qquad \text{(equation 2)}$$

In reality, the total picture of the complex system is given by:

$$2SO_{2(g)} + \text{excess } H_2O_{(l)} \rightleftharpoons 2SO_2 \cdot XH_2O \rightleftharpoons 2H_2SO_3 \rightleftharpoons 2HSO_3^- \begin{cases} \rightleftharpoons 2SO_3^{--} + 2H_3O^+ \\ \rightleftharpoons S_2O_5^{--} + H_2O \end{cases} + 2H_3O^+ \qquad \text{(equation 3)}$$

It can be seen that, in regions of high bisulfite ion concentration, metabisulfite ions will be formed. Since this equilibrium is not considered in the Johnstone equation, the equation is invalid in these regions. It might also be pointed out that the experimental work from which the parameters for the Johnstone equation were derived was done using a transpiration technique. In a transpiration experiment, the P_{SO_2} of a scrubbing liquor is determined by bubbling an inert gas such as nitrogen through the scrubber solution and measuring the mole fractions of the components of the exit gas stream. Thus:

$$P_{SO_2} = \frac{X_{SO_2}}{X_{SO_2} + X_{N_2} + X_{H_2O}} P_T \qquad \text{(equation 4)}$$

where X_i = mole fraction i and

P_T = total pressure

The mole fraction of SO_2 is determined iodometrically and, in order to make a reasonably accurate determination of X_{SO_2}, it is necessary to

transpire a considerable amount of SO_2 from the solution thus causing a considerable uncertainty in the S/C of the liquor. Another large uncertainty is present in X_{H_2O} which is obtained from the Literature values of water vapor pressure, but corrected for the Raoults Law vapor pressure lowering introduced by the ionic strength of the scrubbing liquor. There is much uncertainty as to the actual ionic strength of the liquor, because in a sense this is what is being determined by the total experiment.

Figure 1 shows Johnstone's experimental transpiration data taken at 90°C for the sodium sulfite/bisulfite system at various total sulfur IV concentrations. A semi-log plot of P_{SO_2} versus S/C is shown in this plot. The line through the cluster of points, drawn by the author of this paper to indicate the apparent insensitivity of P_{SO_2} to total sulfur IV concentration, appears to fit the points derived from different S IV concentrations equally well: this contradicts the implications of Henry's Law. Johnstone's equation may be rewritten:

$$P_{SO_2} = MS \left\{ \frac{[2 - 1/(S/C)]^2}{1/(S/C) - 1} \right\} \qquad \text{(equation 5)}$$

Because of the above mentioned inadequacies of the Johnstone equation, it was decided to do a more definitive equilibrium partial pressure experiment which would hopefully yield a more accurate predictive equation for P_{SO_2} as a function of easily measured scurbber liquor parameters.

CONCLUSIONS

An experimental technique has been developed for determining equilibrium partial pressures of sulfur dioxide (P_{SO_2}) over various scrubber liquors. It has been shown that equations developed by H. F. Johnstone[3,4] for equilibrium partial pressure are incorrect.

Experimentally verified theoretical expressions have been developed for P_{SO_2} for strong base (potassium hydroxide and sodium hydroxide) scrubbing systems and also for the buffered sodium citrate scrubbing system. The equations developed are capable of predicting P_{SO_2} from the input parameters--pH, temperature, and concentration of sulfur (IV) in the scrubber liquor. These equations are presented in a form which includes the expected uncertainty of the equations at the 90 percent confidence level.

It is recommended that the equations developed in this paper be used to define maximum thermodynamic control efficiencies achievable for the scrubbing systems studied. Definition of maximum theoretical control efficiency is essential to scrubber design.

It is suggested that the methodologies described in this paper be utilized to develop essential relationships and understandings for other scrubbing systems.

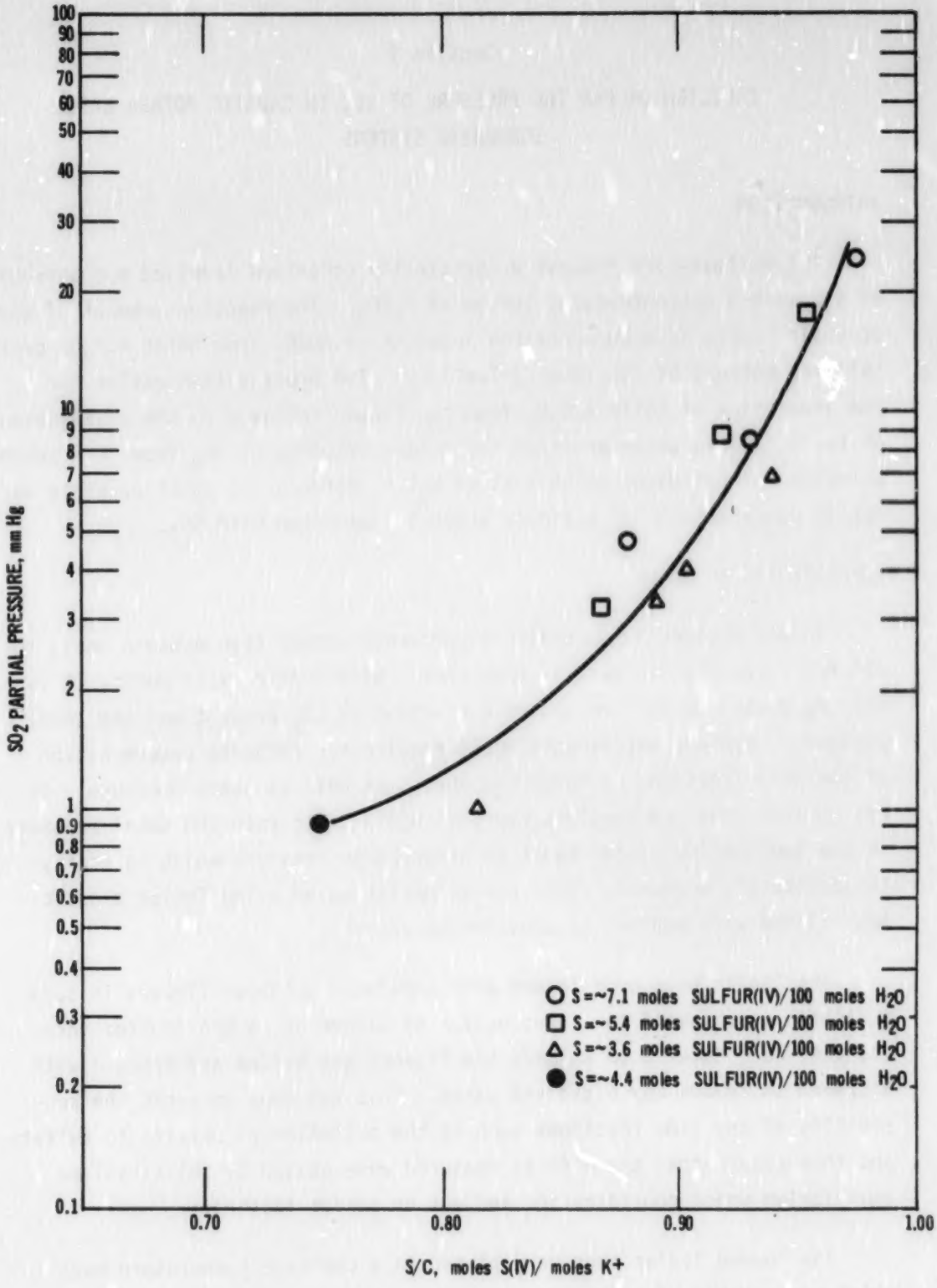

Figure 1. Johnstone's data for $Na_2SO_3/NaHSO_3$ system at 90 °C.

Section I

EQUILIBRIUM PARTIAL PRESSURE OF SO_2 IN CAUSTIC POTASH BASED SCRUBBING SYSTEMS

INTRODUCTION

The Wellman-Lord Process as originally conceived involved the scrubbing of SO_2 with a concentrated solution of K_2SO_3. The reaction product of the scrubbing cycle is a concentrated solution of $KHSO_3$ from which $K_2S_2O_5$ crystallizes because of its lower solubility. The process then called for the separation of solid $K_2S_2O_5$ from the liquor followed by the dissolution of the $K_2S_2O_5$ in water and then the steam-stripping of SO_2 from this second solution. The limited solubility of $K_2S_2O_5$ defines the total possible sulfur IV concentration of a liquor which is saturated with SO_2.

EXPERIMENTAL APPROACH

It was decided to do static experiments rather than dynamic ones, to determine equilibrium partial pressures. With static experiments, it is only necessary to measure the mole fraction of SO_2 present and the total pressure. Dynamic experiments would require the accurate determination of the mole fractions of three components as well as total pressure. It was obvious that the simplest approach would be to keep the total pressure in the equilibrium vessel equal to atmospheric pressure which is easily and accurately measured. This was accomplished by using Tedlar plastic bags fitted with septums as equilibrium vessels.

The Tedlar bags were loaded with simulated scrubber liquors in such a fashion as to avoid the introduction of oxygen or carbon dioxide into the vessels. Water used to make the liquors was boiled and sparged with nitrogen to remove any dissolved gases. This was done to avoid the possibility of any side reactions such as the oxidation of sulfite to sulfate and thus assure that the effects measured were caused by shifts in the equilibrium under consideration and not by random factors.

The loaded Tedlar bags were placed in a constant temperature bath which was capable of controlling the temperature to $\pm$ 0.5°C. It was

determined experimentally that the mole fraction of SO_2 existing in the gas phase in the vessel reached a steady state within 2 hours of the time that the vessel was placed in the bath. The bath itself contained ethylene glycol as the heat exchange medium and was agitated with an air-driven stirrer. The total capacity of each plastic bag was 200 milliliters with each bag containing 150 milliliters of liquor and approximately 50 milliliters of nitrogen.

The gas phase from each equilibrium vessel was analyzed using a Model 990 Perkin-Elmer Gas Chromatograph (G.C.) equipped with a thermal conductivity detector. The G.C. column used was 60 cm x 3.175 mm 316 stainless steel tubing filled with Davidson #12 Silica Gel 60/80 mesh. The flow rate was set at 60 milliliters/minute, the column temperature at 130°C, the detector at 200°C, and the detector current at 275 milliamperes for the determination. Water was removed from the column after the SO_2 peak eluted by raising the column temperature to 195°C for 10 minutes.

Prior to the analysis of the gas phase of the bag for mole fraction of SO_2, the bags were shaken by hand periodically to assure adequate contacting of the gas and liquid phases. The gas samples for G.C. analysis were taken in a 1 cc Hamilton syringe which was heated to the operating temperature of the bath.

The concentration of SO_2 in the gas samples was quantified by comparing the peak height of SO_2 in the sample to the peak height of SO_2 in a 2000 ppm SO_2 in nitrogen span gas standard which was purchased from Matheson. The G.C. analysis procedure was shown experimentally to have a coefficient of variation of 6.9 percent.

Total pressure was measured using a mercury barometer. The SO_2 partial pressure was calculated by the product of total pressure and mole fraction SO_2.

pH readings were taken on samples of liquor after the gas phase was analyzed. These readings were taken on a temperature-compensated, expanded-scale pH meter using a combination Ag-AgCl/glass electrode.

Samples of the liquor were also titrated iodometrically for total sulfur IV to confirm that the weighing and transfer of solid reagents was quantitative.

Levels of Parameters Utilized

It was decided that the sulfur IV concentration of the liquors which were to be studied by this experiment would be defined by the solubility of $K_2S_2O_5$ at the various temperature levels. Accordingly, sulfur IV concentrations were held at as many as three levels for each temperature level. These levels were arbitrarily chosen as fully saturated, half saturated, and one-fifth saturated with respect to $K_2S_2O_5$.

Supplemental measurements were made to determine experimentally the solubility of $K_2S_2O_5$ in de-oxygenated water as a function of temperature. The results of these measurements are shown in Figure 2. These measurements were made by saturating solutions of $K_2S_2O_5$ at various temperatures and determining sulfur IV iodometrically.

The experimentally determined solubilities are lower than those quoted by Linke[5]. The solubilities quoted by Linke are shown as the dashed line on Figure 2. The difference might possibly be due to the de-gasing of the water used in this experiment. The presence of dissolved oxygen could cause oxidation of $K_2S_2O_5$ to K_2SO_4, a more soluble compound.

The simulated scrubber liquors were made for a given experimental run by using a mixture of $K_2S_2O_5$ and K_2SO_3 to adjust the S/C's of the liquors over the S/C range 0.5 to 1.0 but holding S, the total sulfur IV concentration, constant for all solutions of a given run. P_{SO_2} and pH were measured for each liquor as described previously.

Data was taken for liquors at three different temperatures, chosen both to bracket the typical operating temperature of a scrubber, and also to approach the temperature at which steam stripping would take place. The typical temperature of an operating scrubber is 50°C and the typical temperature of the steam stripper is approximately 100°C. The raw data for the $KHSO_3/K_2SO_3$ system is presented in Table 1.

DISCUSSION OF DATA

In order to compare the experimental data with the Johnstone equation, P_{SO_2} in mm of mercury was plotted against S/C on semi-log plots in Figures 3 through 9. A computer program, written for the Johnstone equation, was

Table 1. EQUILIBRIUM DATA FOR $KHSO_3/K_2SO_3$ SYSTEM

Molarity Sulfur IV	S/C	P_{SO_2} mmHg	pH	Temperature, °K
1.82	0.99	1.25	4.6	298
1.82	0.98	0.381	5.0	298
1.82	0.97	0.194	5.2	298
1.82	0.96	0.138	5.35	298
1.82	0.94	0.066	5.5	298
3.66	0.99	1.32	4.8	298
3.66	0.98	0.45	5.15	298
3.66	0.97	0.23	5.3	298
3.66	0.94	0.065	5.7	298
3.66	0.90	0.068	6.0	298
0.882	0.99	2.19	4.7	323
0.882	0.98	1.09	5.1	323
0.882	0.96	0.30	5.4	323
0.882	0.92	0.14	5.75	323
2.48	0.99	5.62	4.7	323
2.48	0.98	2.21	5.0	323
2.48	0.94	0.634	5.55	323
2.48	0.80	0.070	6.3	323
4.98	0.99	6.27	4.95	323
4.98	0.98	2.57	5.3	323
4.98	0.94	0.701	5.9	323
4.98	0.88	0.351	6.36	323
1.14	0.98	5.49	5.05	348
1.14	0.94	1.19	5.6	348
1.14	0.88	0.27	6.0	348
3.06	0.99	17.9	4.8	348
3.06	0.98	8.74	5.1	348
3.06	0.94	2.04	5.65	348
3.06	0.88	0.656	6.0	348
3.06	0.80	0.210	6.4	348
6.12	0.99	21.1	4.9	348
6.12	0.98	9.61	5.3	348
6.12	0.94	2.16	6.0	348
6.12	0.88	0.625	6.35	348
6.12	0.80	0.155	6.9	348

used to define the dashed lines on these plots. Johnstone did not give an equation for "M" for the potassium system; therefore, his equation developed for the sodium system was used:

$$\log M = 4.619 - 1987/T \qquad \text{(equation 6)}$$

The assumption that the equation for the sodium system may be used for the potassium system can be rationalized on the basis that sodium and potassium hydroxides are both very strong bases and are completely ionized in aqueous solutions.

An examination of Figures 3 through 9 reveals very little similarity between the data of this work and the line calculated from the Johnstone equation. It can be seen that on any given plot, the ratio between the data and the line calculated from the Johnstone equation is not constant. The differences between the data and the Johnstone equation cannot therefore be resolved by an adjustment of the "M" term of the Johnstone equation. In all cases except for that shown on Figure 7, the Johnstone equation predicts partial pressures which are high when compared to the data. Although, the Johnstone equation is actually a fairly good fit of the data shown on Figure 7, the fit is probably just coincidence.

The practical implications of the differences between the data and the Johnstone model follow.

First, the actual SO_2 removal in a K_2SO_3 scrubber which operates at equilibrium should be better at any given S/C than that predicted by the Johnstone equation. Secondly, the data predict that the steam requirements, for the stripping of SO_2 from the pregnant liquor and the resultant regeneration of the liquor, will be higher than those predicted using the Johnstone model. This would have a significant effect upon the economics of the total scrubbing process.

In an attempt to relate partial pressures to the solution parameters in a simple straightforward manner, the experimental P_{SO_2}'s were plotted against pH on semi-log paper. These plots are shown in Figures 10 through 12. As would be expected, these plots show a straight line relationship which can be expressed mathematically by the use of a least squares fit of the data.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing) PB-261 914

1. REPORT NO. EPA-600/2-76-279	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: Equilibrium Partial Pressure of Sulfur Dioxide in Alkaline Scrubbing Processes	5. REPORT DATE: October 1976
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): David K. Oestreich	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Chemical Processes Branch, Industrial Processes Division, IERL-RTP, Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.: 1AB013; ROAP 21ADE
	11. CONTRACT/GRANT NO.: NA
12. SPONSORING AGENCY NAME AND ADDRESS: EPA, Office of Research and Development, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED: In-house; 1970-71 (Lab Work)
	14. SPONSORING AGENCY CODE: EPA-ORD
15. SUPPLEMENTARY NOTES	

16. ABSTRACT: The report gives results of IERL-RTP in-house studies in which equilibrium partial pressure of SO2 was measured as a function of pH, temperature, and concentration of sulfur (IV) on various scrubber liquors. These studies were done for potassium-, sodium-, and citrate-based scrubbing systems. It is shown that equations developed by earlier workers for predicting SO2 partial pressures are incorrect. Theoretical expressions are developed to relate the equilibrium partial pressure of SO2 to the important scrubber parameters. These expressions are experimentally validated at the 90 percent confidence level.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Flue Gases	Stationary Sources	21B
Scrubbers	Alkaline Scrubbing	07A 07C
Sulfur Dioxide	Equilibrium Partial Pressure	07B
Equilibrium Partial Pressure		07D
Potassium		
Sodium		
Citrates		

18. DISTRIBUTION STATEMENT: Unlimited	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 41
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: $4.00/3.00

EPA Form 2220-1 (9-73)

The least squares straight line fits of the data shown in Figures 10 through 12 appear generally to fit the data quite well. An exception to this is the data point occurring at the lowest pH for each run. As pH's drop from about 4.25 to 4.00, the line inexplicably turns over. Consequently, the initial data point for each run was dropped for the least squares analysis.

The anomaly at low pH's is very possibly due to equilibria other than the first ionization of sulfurous acid coming into prominence. The formation of metabisulfite is known to be enhanced at low pH's.

DEVELOPMENT OF THEORETICAL MODEL AND PREDICTIVE EQUATION FOR PARTIAL PRESSURE

As a first approximation, if one considers the chemical equilibria of interest as given in equation (3), within the pH range of interest, the only equilibrium of great importance is the first ionization constant of sulfurous acid:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$K_1 = \frac{[H^+]\,[HSO_3]}{[H_2SO_3]} = 1.7 \times 10^{-2} \qquad \text{(equation 7)}$$

For all practical purposes, the total S(IV) concentration in solution is equal to the sum of the sulfurous acid concentration and the bisulfite ion concentration. Thus with substitution:

$$K_1 = \frac{[H^+]\left\{[S(IV)] - [H_2SO_3]\right\}}{[H_2SO_3]} \qquad \text{(equation 8)}$$

Solving this expression for $[H_2SO_3]$, one obtains:

$$[H_2SO_3] = \frac{[H^+]\;[S(IV)]}{K_1 + [H^+]} \qquad \text{(equation 9)}$$

In the denominator of equation 9, it is seen that within the pH range of interest, $[H^+]$ is inconsequentially small compared to K_1 and may be

dropped. (At a pH of 3, $[H^+] = 1 \times 10^{-3}$ which is 6 percent of K_1 and as pH rises $[H^+]$ rapidly becomes smaller.)

Thus:

$$[H_2SO_3] = \frac{[H^+]\,[S(IV)]}{K_1} = \frac{[S(IV)]\,e^{-2.303\ pH}}{K_1} \qquad \text{(equation 10)}$$

Henry's Law states that

$$P_{SO_2} = K_h\,[H_2SO_3] \qquad \text{(equation 11)}$$

where K_h is the Henry's Law constant.

Substitution of equation (10) into equation (11) yields:

$$P_{SO_2} = K\,[S(IV)]\,e^{-2.303\ pH} \qquad \text{(equation 12)}$$

where $K = K_h/K_1$.

The integrated form of the van't Hoff Equation may be used to relate equilibrium constant to absolute temperature and has the form:

$$\ln K = \frac{a(1000)}{T} + b. \qquad \text{(equation 13)}$$

Taking the data for the potassium sulfite/potassium bisulfite system given in Table 1, K may be calculated using equation (12) for each data point. A least squares fit may then be done for the coefficients a and b from equation (13) using calculated K and measured T for each data point. The resulting equation for K using the regression analysis coefficients is:

$$\ln K = \frac{-5.77(1000)}{T} + 29.24 \qquad \text{(equation 14)}$$

Equation (14) may be manipulated and substituted into equation (12) to yield:

$$P_{SO_2} = [S(IV)]\ \exp\left\{-2.303pH - \frac{5.77(1000)}{T} + 29.24\right\} \qquad \text{(equation 15)}$$

In the approach taken above, since K is determined empirically from a theoretical expression which employs measured data, all the uncertainty existing in the data is translated to an uncertainty in K. The uncertainty in K is further translated to an uncertainty in the coefficient -5.77 of equation (14). This uncertainty was calculated at the 90 percent confidence level using Student's t distribution. Thus equation (14) becomes at the 90 percent confidence level:

$$\ln K = \frac{-(5.77 \pm 0.17\ (1000)}{T} + 29.24 \qquad \text{(equation 16)}$$

and equation (15) becomes:

$$P_{SO_2} = [S(IV)] \exp \left\{-2.303pH - \frac{(5.77 \pm 0.17)(1000)}{T} + 29.24\right\} \qquad \text{(equation 17)}$$

A comparison of experimental P_{SO_2} values with P_{SO_2} values calculated using equation (17) is given in Table 2. The lower and upper calculated values are given for the 90 percent confidence level. Out of the 34 data points shown in the table, five experimental P_{SO_2}'s are out of limits whereas the confidence level predicts statistically that 3.4 data points will be out of limits.

Equation (17) is demonstrated to be quite usable for engineering purposes, and far superior to the Johnstone Equation. It should, however, be remembered that the assumptions made in developing equation (17) limit the pH range in which the equation is useful. At pH's lower than 3.5 and higher than 6.0 the equation becomes less exact.

Table 2. COMPARING EXPERIMENTAL P_{SO_2} (EP_{SO_2}) WITH VALUES CALCULATED FROM EQUATION (17)

[S(IV)], M	pH	T, °K	Exper. P_{SO_2} mmHg	P_{SO_2} Calculated for 90% Confidence Level, mmHg		
				Lower	Expected	Upper
1.82	4.65	298.00	1.25	0.45	0.79	1.40
1.82	5.00	298.00	0.38	0.20	0.35	0.63
1.82	5.20	298.00	0.19	0.13	0.22	0.40
1.82	5.35	298.00	0.14	0.09	0.16	0.28
1.82	5.50	298.00	0.07	0.06	0.11	0.20
3.66	4.80	298.00	1.32	0.64	1.13	2.00
3.66	5.15	298.00	0.45	0.28	0.50	0.89
3.66	5.30	298.00	0.23	0.20	0.36	0.63
3.66	5.70	298.00	0.07	0.08[a]	0.14[a]	0.25
0.88	4.70	323.00	2.19	0.91	1.53	2.59
0.88	5.10	323.00	1.09	0.36[a]	0.61[a]	1.03[a]
0.88	5.40	323.00	0.30	0.18	0.31	0.52
0.88	5.75	323.00	0.14	0.08	0.14	0.23
2.48	4.70	323.00	5.62	2.54	4.31	7.29
2.48	5.00	323.00	2.21	1.28	2.16	3.65
2.48	5.55	323.00	0.63	0.36	0.61	1.03
2.48	6.30	323.00	0.07	0.06	0.11	0.18
4.98	4.95	323.00	6.27	2.87	4.86	8.23
4.98	5.30	323.00	2.57	1.28	2.17	3.68
4.98	5.90	323.00	0.70	0.32	0.55	0.92
4.98	6.36	323.00	0.35	0.11[a]	0.19[a]	0.32[a]
1.14	5.05	348.00	5.49	1.96[a]	3.19[a]	5.20[a]
1.14	5.60	348.00	1.19	0.55	0.90	1.47
1.14	6.00	348.00	0.27	0.22	0.36	0.58
3.06	4.80	348.00	17.90	9.35	15.23	24.83
3.06	5.10	348.00	8.74	4.68	7.63	12.44
3.06	5.65	348.00	2.04	1.32	2.15	3.51
3.06	6.00	348.00	0.66	0.59	0.96	1.57
3.06	6.40	348.00	0.21	0.23[a]	0.38[a]	0.62[a]
6.12	4.90	348.00	21.10	14.85	24.20	39.45
6.12	5.30	348.00	9.61	5.91	9.63	15.70
6.12	6.00	348.00	2.16	1.18	1.92	3.13
6.12	6.35	348.00	0.63	0.53	0.86	1.40
6.12	6.90	348.00	0.16	0.15	0.24	0.39

[a]Equation failure

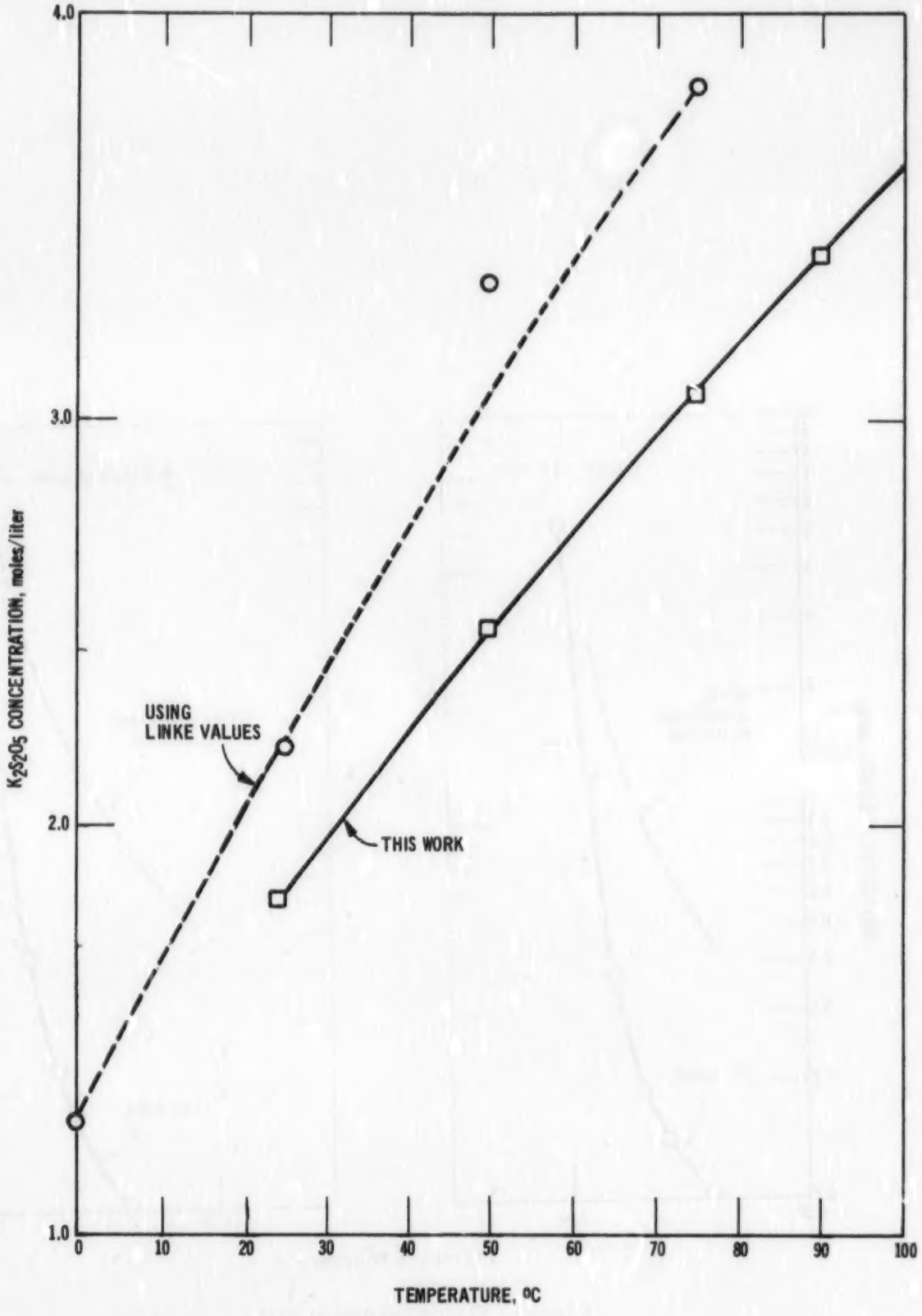

Figure 2. Solubility of $K_2S_2O_5$ in oxygen-free water.

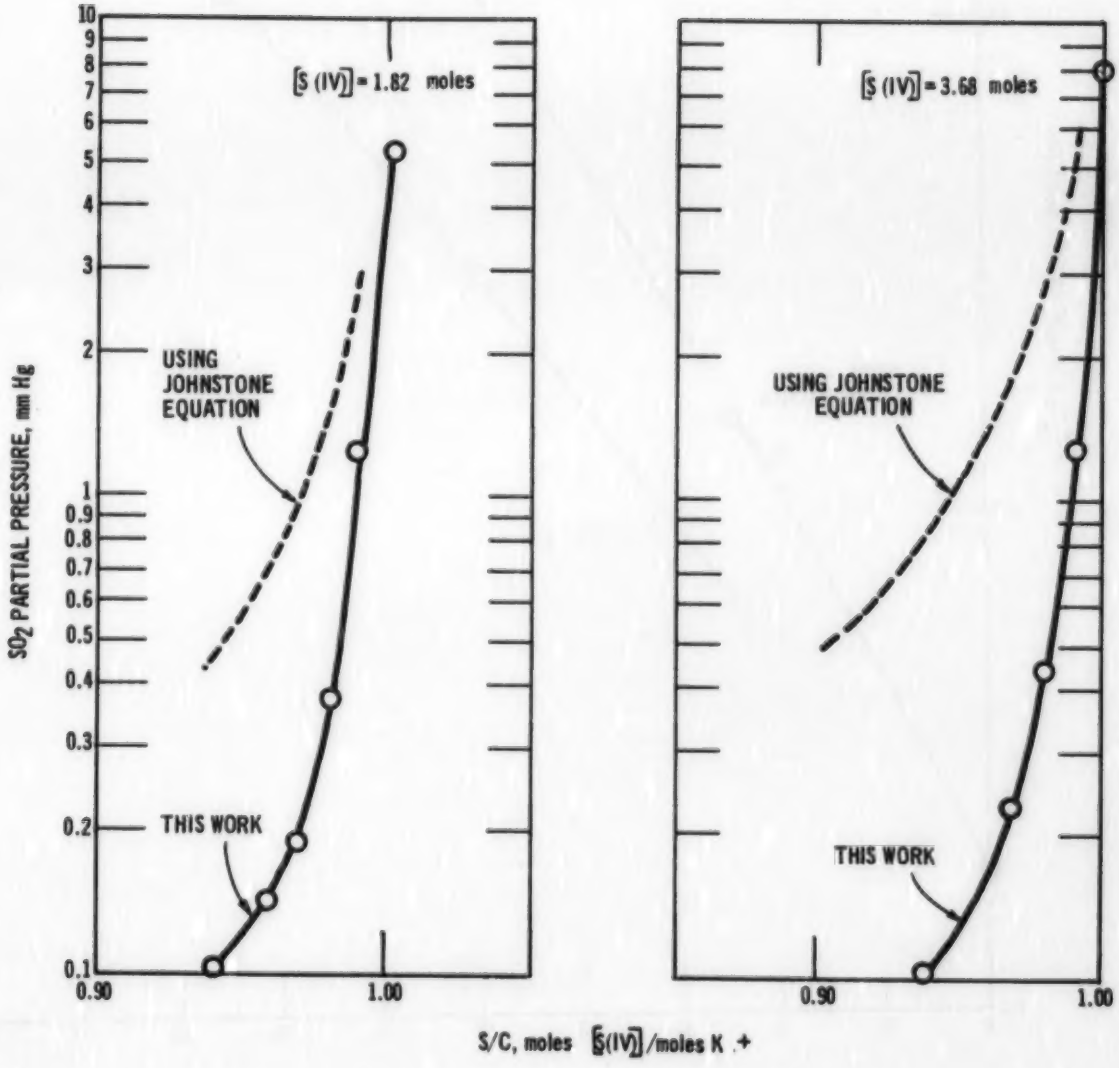

Figure 3. Equilibrium data at 25 °C.

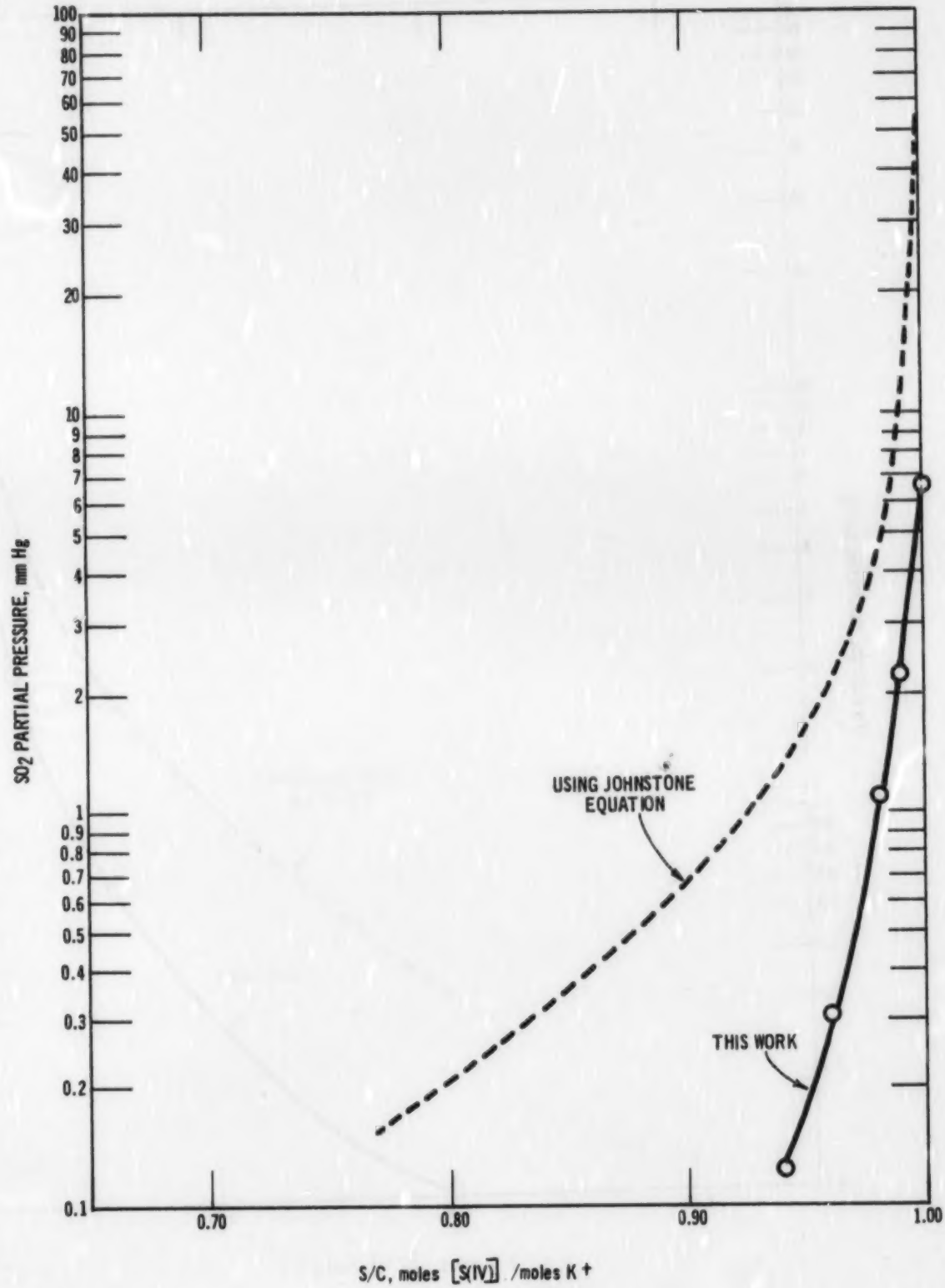

Figure 4. Equilibrium data for [S(IV)] = 0.88 molar at 50 °C.

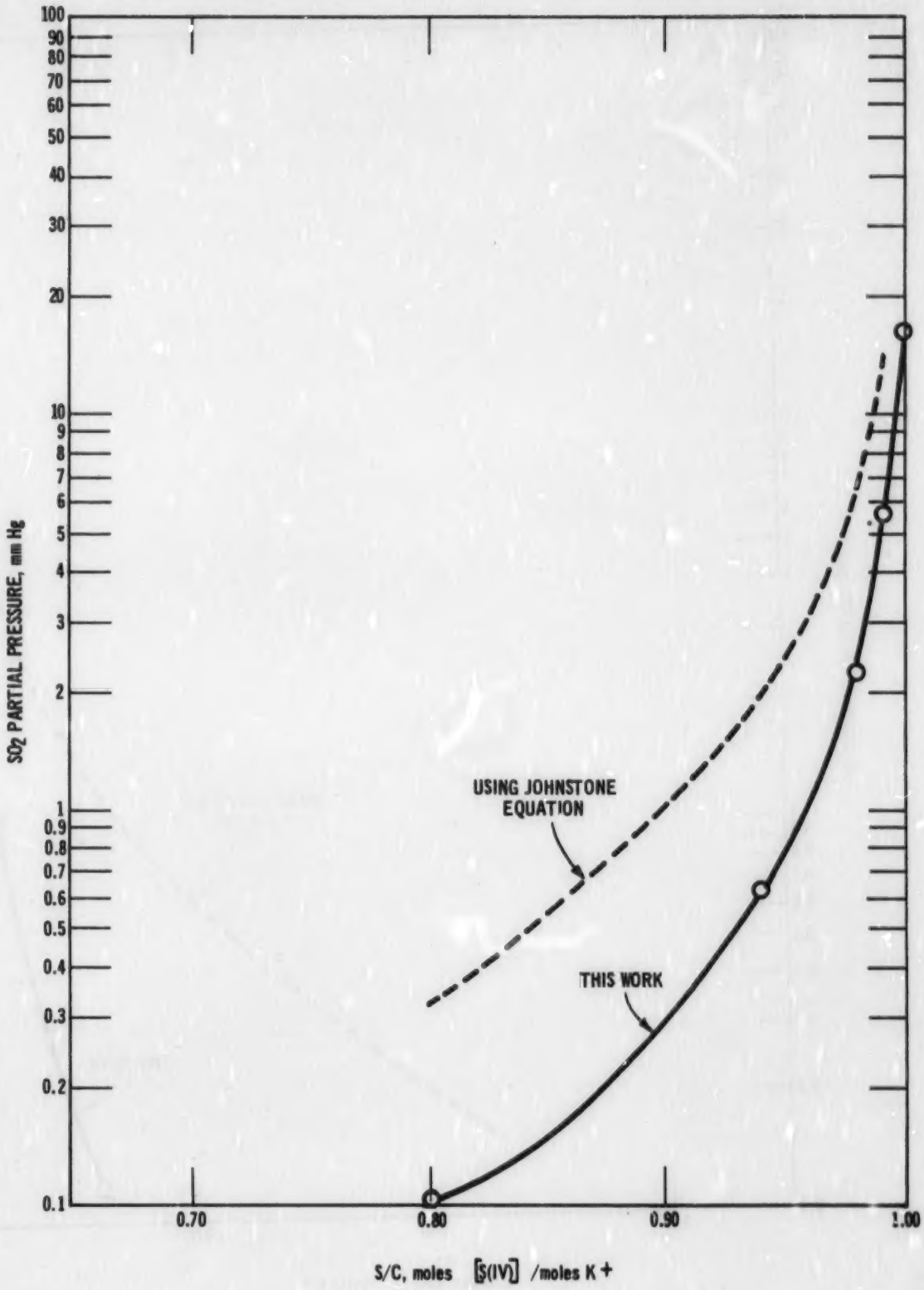

Figure 5. Equilibrium data for [S(IV)] = 2.48 molar at 50 °C.

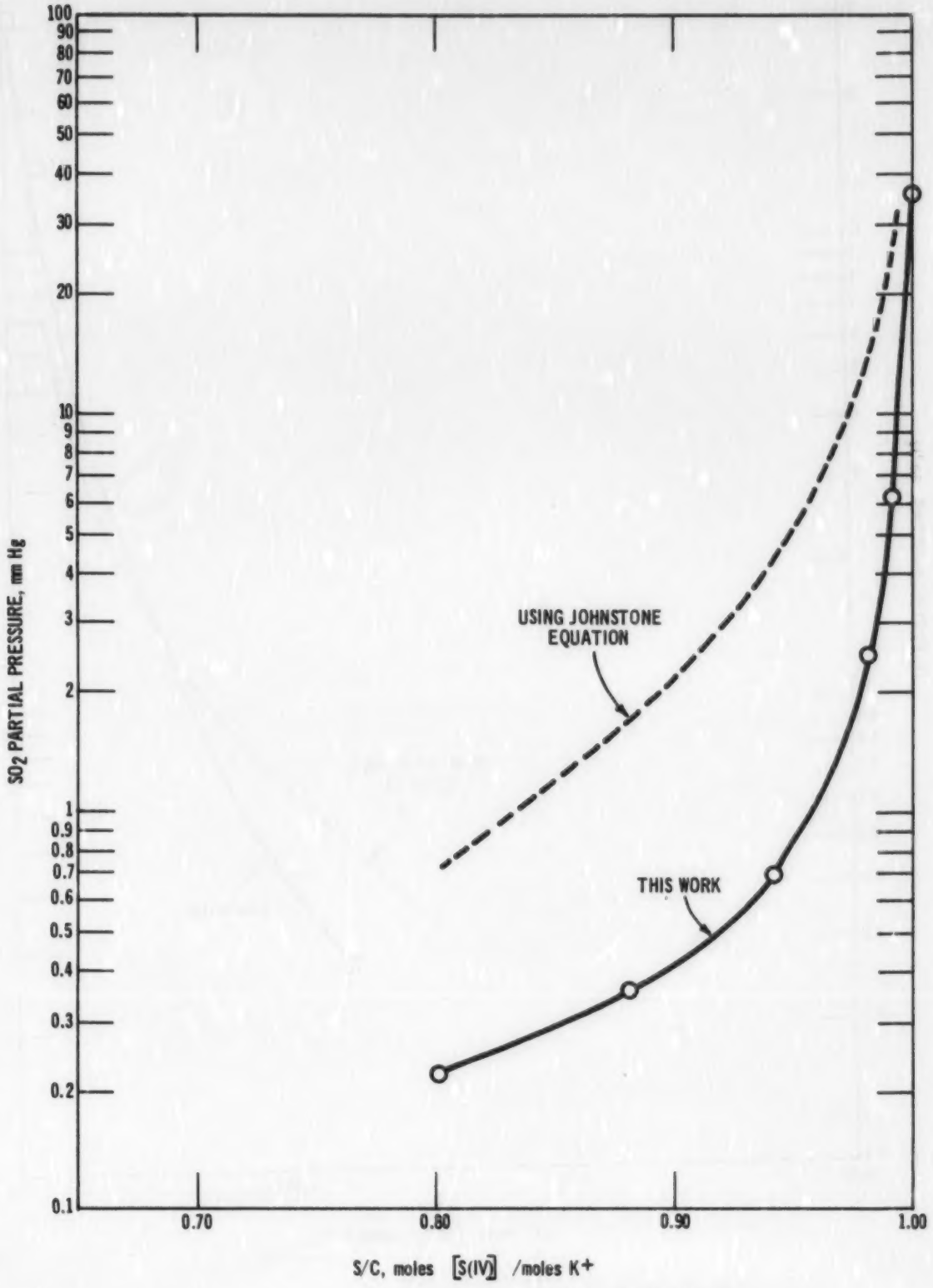

Figure 6. Equilibrium data for [S(IV)] = 4.98 molar at 50 °C.

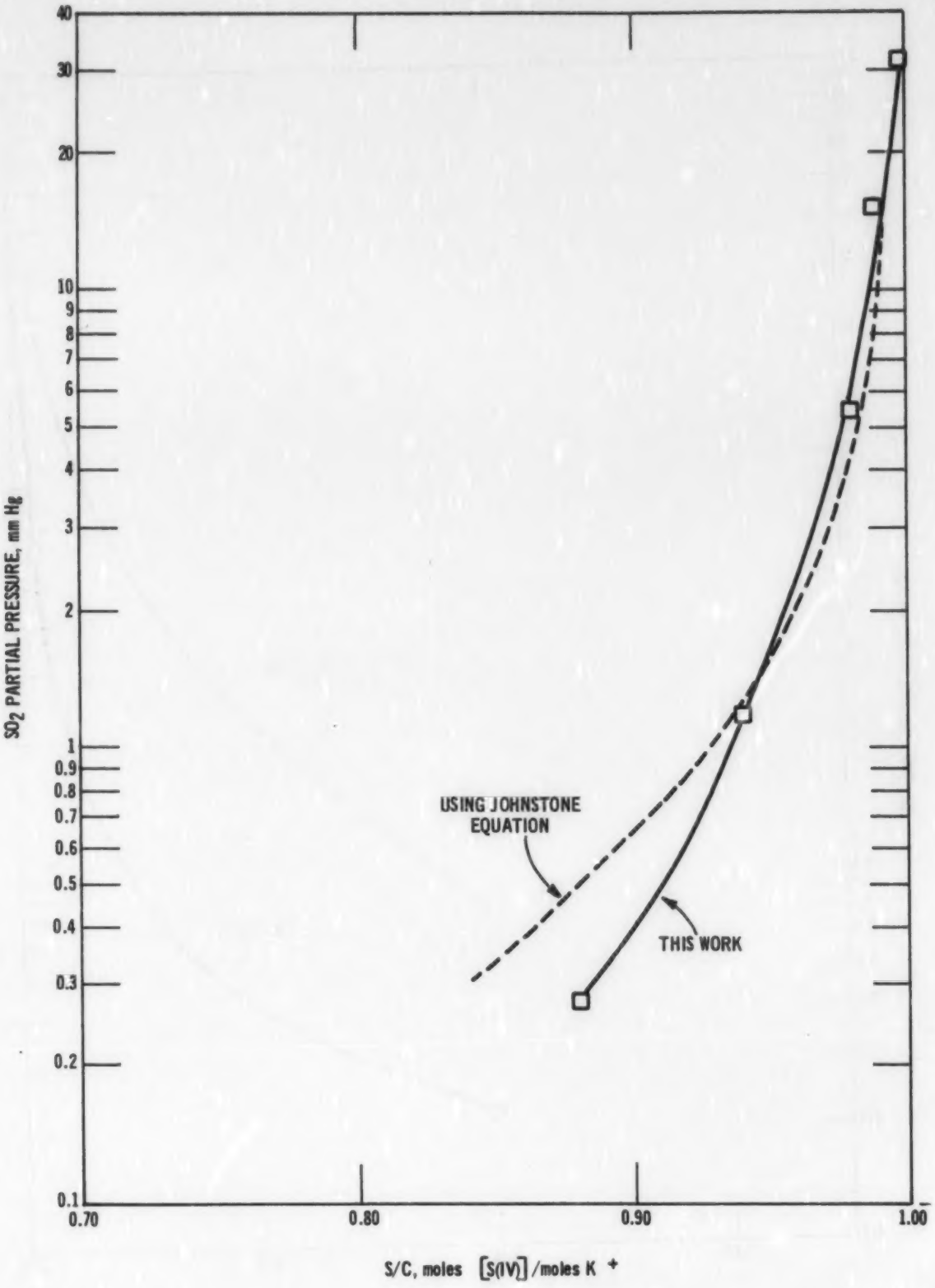

Figure 7. Equilibrium data for [S(IV)] = 1.14 molar at 75 °C.

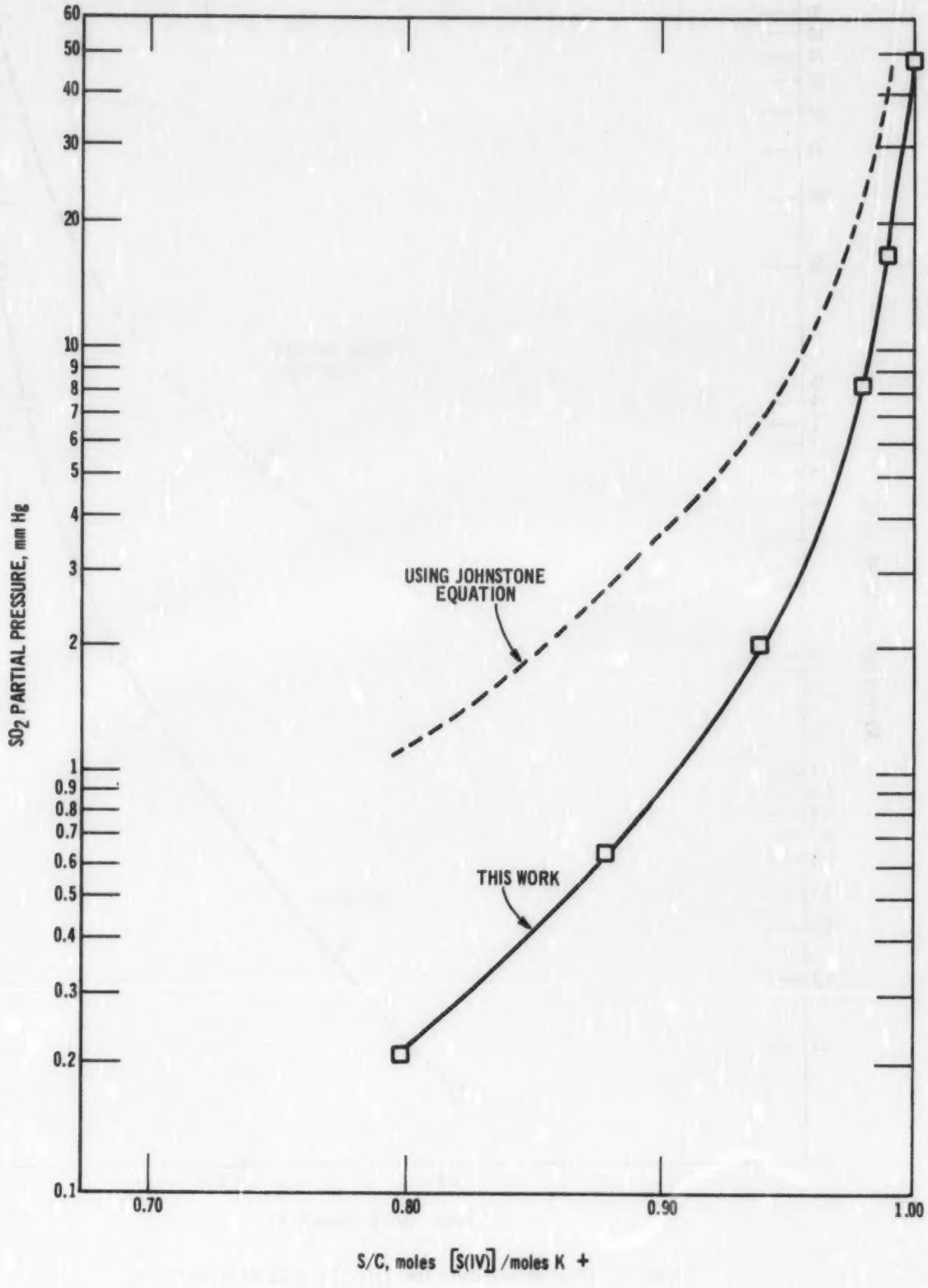

Figure 8. Equilibrium data for [S(IV)] = 3.06 molar at 75 °C.

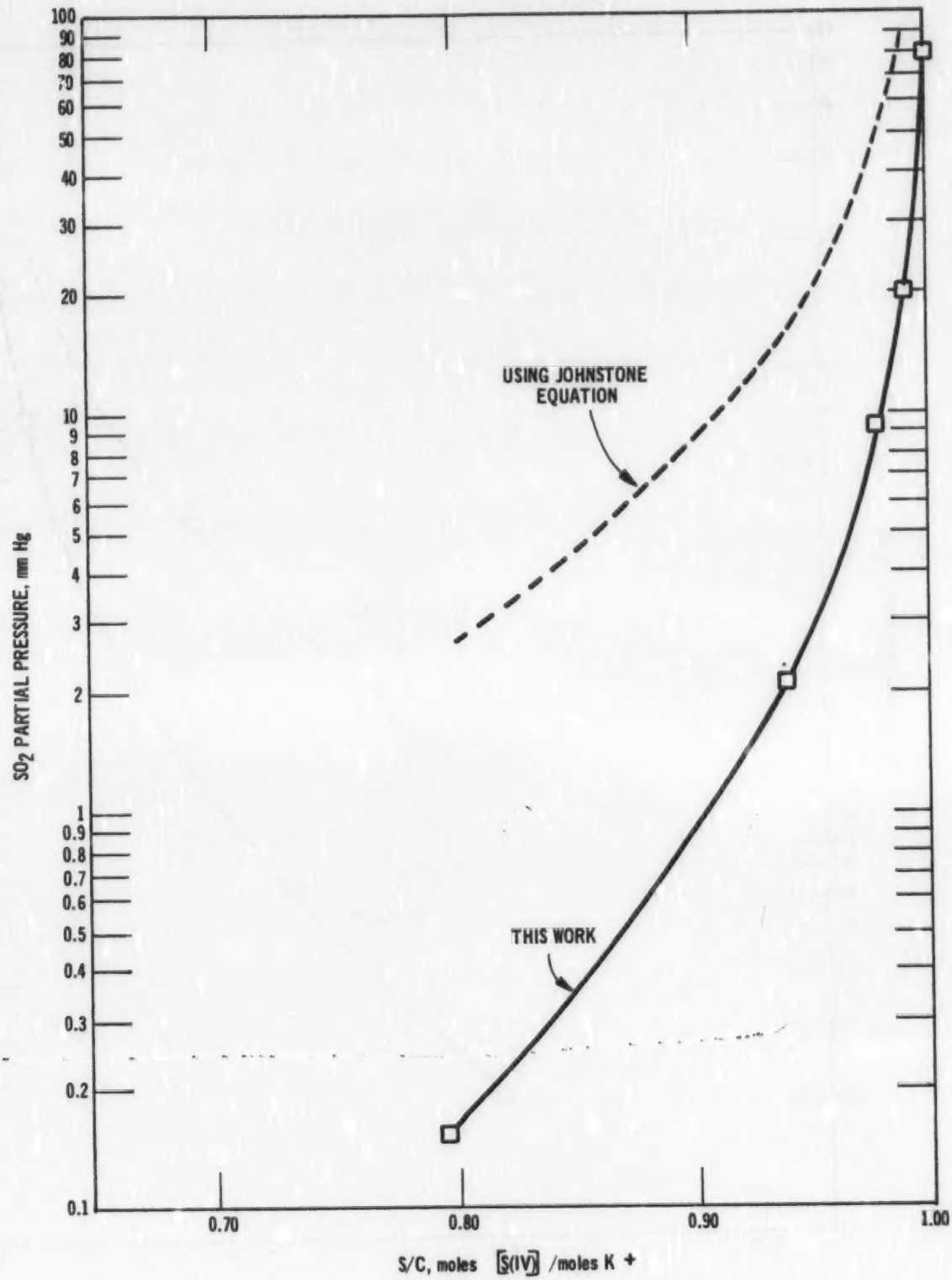

Figure 9. Equilibrium data for [S(IV)] = 6.12 molar at 75 °C.

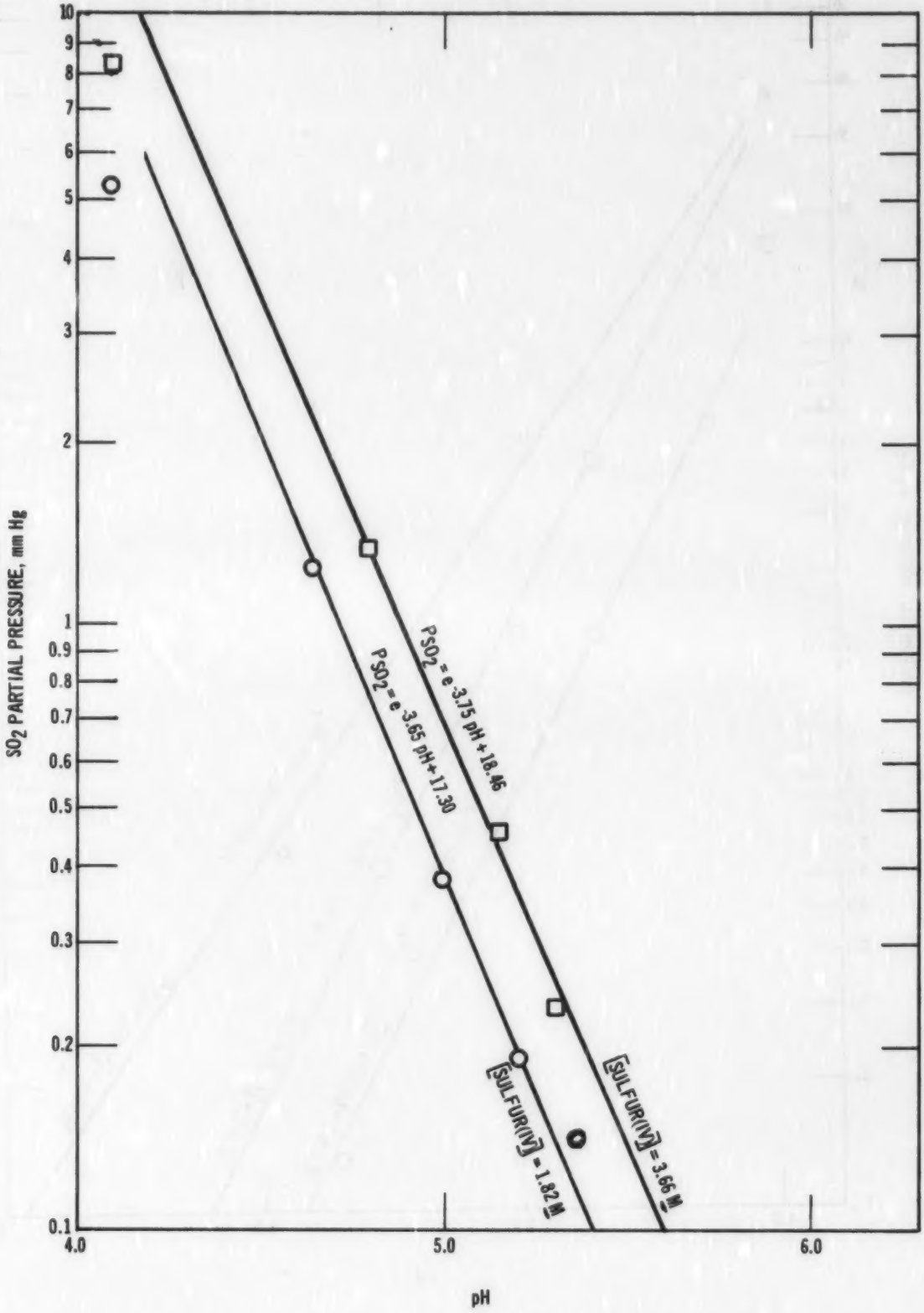

Figure 10. Equilibrium data at 25 °C.

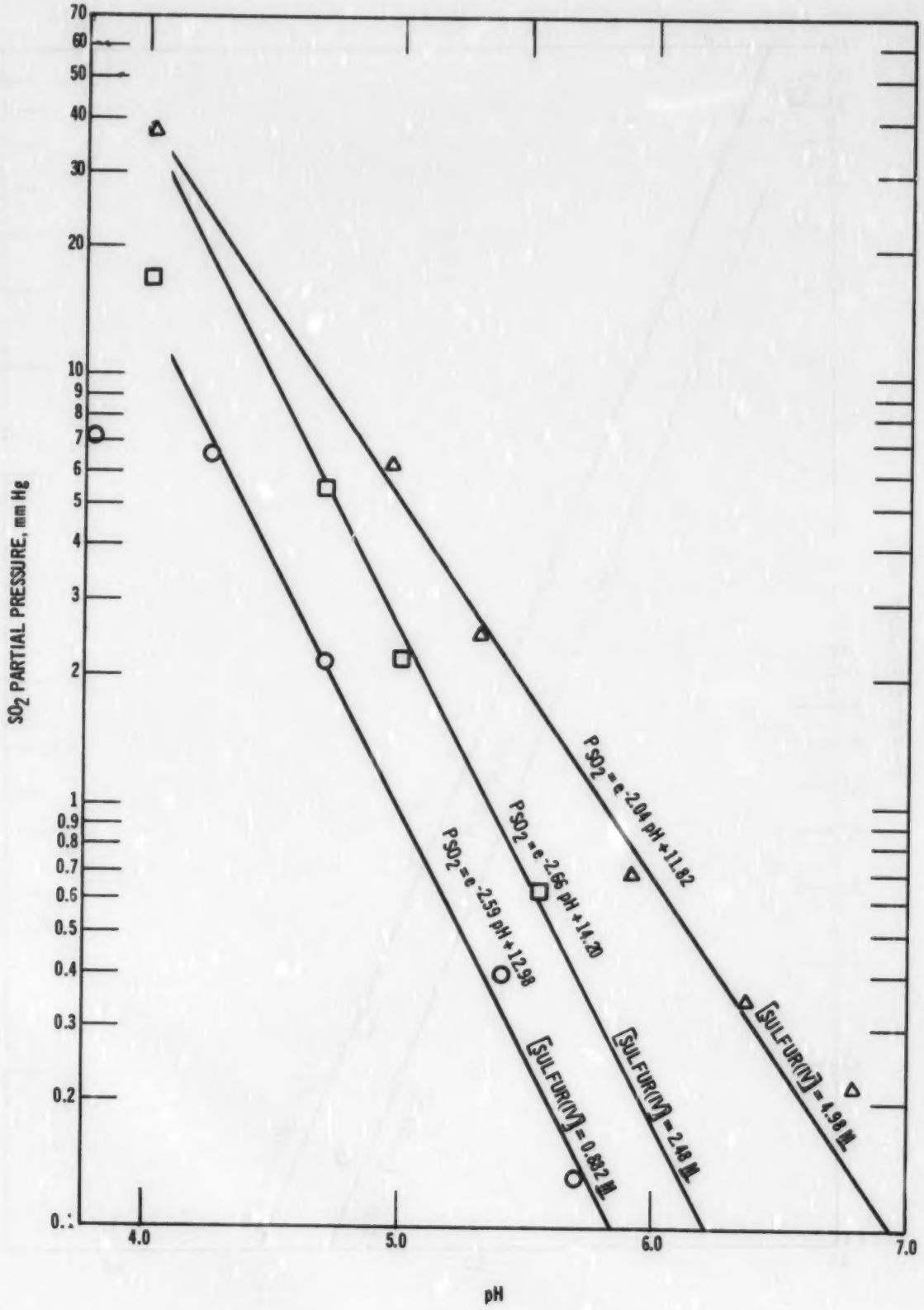

Figure 11. Equilibrium data at 50 °C.

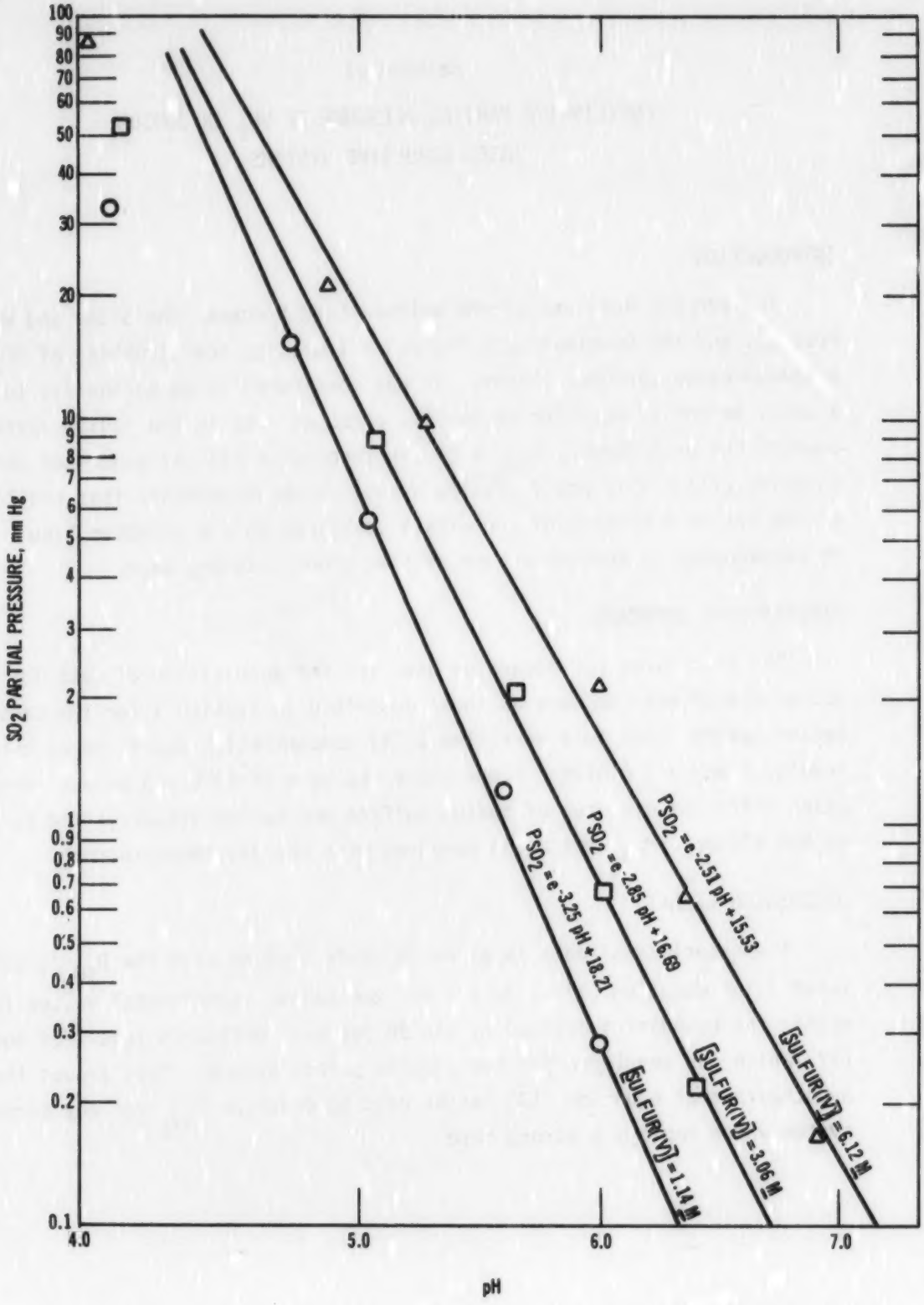

Figure 12. Equilibrium data at 75 °C.

Section II

EQUILIBRIUM PARTIAL PRESSURE OF SO_2 IN SODIUM BASED SCRUBBING SYSTEMS

INTRODUCTION

The present versions of the Wellman-Lord Process, the Stone and Webster Process, and the Double-Alkali Process all utilize the scrubbing of SO_2 with a sodium-based scrubber liquor. It was considered to be worthwhile to take a small amount of equilibrium partial pressure data in the sodium system to compare the experimental P_{SO_2}'s to the theoretical values generated using equation (17). This would provide a test of the hypothesis that the identity of the cationic portion of the alkali contained in the scrubber liquor is of no consequence as long as we are talking about a strong base.

EXPERIMENTAL APPROACH

The procedures and apparatus used for the acquisition of data for the sodium system are the same as those described in Section I for the caustic potash system. For this work, the S(IV) concentration was fixed at two levels, 2.96M and 6.012M. Temperature was held at 50°C and pH was varied using different mixtures of sodium sulfite and sodium metabisulfite to make up the liquor. P_{SO_2} was again measured with the gas chromatograph.

DISCUSSION OF DATA

The experimental data is given in Table 3 along with the P_{SO_2}'s calculated using equation (17). In all but two cases, experimental values fall within the boundaries defined by the 90 percent confidence level for equation (17) which was developed for the caustic potash system. This proves the hypothesis that equation (17) can be used to describe P_{SO_2} for any scrubbing system which employs a strong base.

Table 3. P_{SO_2} EQUILIBRIUM DATA FOR SODIUM BASED SCRUBBER LIQUOR[a]

[S(IV)], M	pH	Exper. P_{SO_2} mmHg	P_{SO_2} Calculated for 90% Confidence Level		
			Lower	Expected	Upper
6.012	4.05	73.1	27.6	46.6	79.0
6.012	4.50	23.7	9.78	16.5	28.0
6.012	4.75	11.2	5.50	9.30	15.7
6.012	5.33	3.58	1.45	2.45	4.14
6.012	5.5	1.63	0.98	1.65	2.80
6.012	5.63	b	0.72	1.23	2.07
2.96	4.18	31.5	10.1	17.0	28.8
2.96	4.52	12.1	4.60	7.78	13.2
2.96	4.8	5.52	2.41	4.08	6.91
2.96	5.3	2.43	0.76	1.29	2.18
2.96	5.67	0.44	0.33	0.55	0.93
2.96	5.98	0.20	0.16	0.27	0.46

[a] Temperature = 323°K

[b] Sample lost

SECTION III

EQUILIBRIUM PARTIAL PRESSURE OF SO_2 IN SODIUM CITRATE BASED SCRUBBING SYSTEMS

INTRODUCTION

It has long been considered that a scrubbing system which is based on a buffer system other than the sulfite/bisulfite system would offer considerable advantage by minimizing the troublesome oxidation of S(IV) to S(VI). The U. S. Bureau of Mines (USBM) has developed a process based on the sodium citrate buffer system[2] through the pilot plant stage. At a pH of 3.7 the scrubbing reaction probably is:

$$SO_2 + H_2O + H_2Cit^- \rightleftharpoons HSO_3^- + H_3Cit \qquad \text{(equation 18)}$$

(In reference (2), the USBM postulated the formation and existence of an intermediate complex between bisulfite and citric acid; however, the data of this work does not support the contention.)

The bulk of the USBM data, showing the equilibrium SO_2 concentration of the gas phase as a function of the S(IV) concentration in the scrubber liquor and temperature, was taken for P_{SO_2}'s which are much higher than the inlet concentrations would be for power plant flue gas.

It is of interest to consider the possible application of the citrate process to power plant flue gases having SO_2 concentrations of approximately 3000 ppm. The maximum removal efficiency is defined by the equilibrium partial pressure of SO_2 for a given set of liquor parameters.

EXPERIMENTAL APPROACH

The basic mechanics of conducting a static equilibrium partial pressure experiment were discussed in Section I with reference to the caustic potash based scrubbing system. The same apparatus was used for the citrate scrubbing system work.

For this work, the liquor concentrations for [S(IV)] and citric acid were set at approximately the same levels corresponding to inlet gas SO_2 concentrations of ~2500 ppm which are indicated in the USBM work. Thus, the liquor sulfur (IV) loading was fixed at two levels --0.0264M and 0.0557M-- which are equivalent to 1.69 and 3.57 g SO_2/liter, respectively. The citrate concentration was fixed at 0.834M. The pH was varied over the range of interest by the addition of different amounts of solid sodium hydroxide. Three levels of temperature were chosen-- 303, 323, and 348°K-- to bracket the range of interest.

DISCUSSION OF DATA

The raw data obtained from this effort are given in Table 4.

Individual runs are presented as semi-log plots of P_{SO_2} versus pH for various temperatures in Figure 13. The lines drawn through the data points are defined by least squares analysis of the data and the equations given utilize the coefficients of the regression analysis.

The effect of total citrate concentration was not studied experimentally; however, it can be seen from the USBM work that at a given mole ratio of H_3 Cit to NaH_2 Cit, the effect of raising the total citrate concentration only increases the buffer's capacity to resist a change in pH. As the capacity of the buffer is increased, the capacity of the liquor for S(IV) increases.

Thus, holding the total citrate concentration constant, it is found that P_{SO_2} is a function of pH, [S(IV)], and temperature. This relationship has the same form as equation (12) developed for the caustic potash system:

$$P_{SO_2} = K\,[S(IV)]\,e^{-2.303\ pH} \qquad \text{(equation 12)}$$

where:

$$\ln K = \frac{a(1000)}{T} + b \qquad \text{(equation 13)}$$

The coefficients a and b were again calculated by doing a least squares fit of the K's calculated for each data point using equation (12). The resulting expression for the equation at the 90 percent confidence level is:

$$\ln K = -(8.20 \pm 0.23)\,\frac{(1000)}{T} + 37.57 \qquad \text{(equation 19)}$$

Table 4. EQUILIBRIUM DATA FOR THE SYSTEM SO_2--CITRIC ACID--NaOH-H_2O

[S(IV)], M	pH	T, °K	Exper. P_{SO_2} mmHg
0.0264	3.57	323.00	1.35
0.0264	3.65	323.00	0.96
0.0264	3.83	323.00	0.70
0.0264	4.02	323.00	0.45
0.0264	4.11	323.00	0.28
0.0264	4.25	323.00	0.17
0.0264	3.50	348.00	8.84
0.0264	3.69	348.00	7.59
0.0264	3.80	348.00	4.79
0.0264	4.00	348.00	3.89
0.0264	4.10	348.00	2.22
0.0264	4.18	348.00	1.43
0.0264	4.26	348.00	1.01
0.0557	3.65	348.00	20.15
0.0557	3.78	348.00	16.60
0.0557	3.84	348.00	11.50
0.0557	3.92	348.00	8.99
0.0557	4.10	348.00	7.12
0.0557	4.24	348.00	4.92
0.0557	4.33	348.00	3.52
0.0557	3.30	303.00	1.39
0.0557	3.52	303.00	0.98
0.0557	3.65	303.00	0.65
0.0557	3.72	303.00	0.38
0.0557	3.85	303.00	0.27
0.0557	4.00	303.00	0.20
0.0557	4.10	303.00	0.12

The equation for partial pressure becomes:

$$P_{SO_2} = [S(IV)] \exp \left\{-2.303pH - (8.20 \pm 0.23) \frac{(1000)}{T} + 37.57\right\} \quad \text{(equation 20)}$$

Please note that equation (20) is valid only for a total citrate concentration of 0.834 M. The coefficients for equation (19) may be different for different total citrate concentrations.

It can be observed that the coefficients a and b for the caustic potash system are quite different from the coefficients derived for the citrate system. This can be expected not only for the reasons given above, but also because the two experiments represent large differences in the ionic strengths of the scrubber liquors. These differences in ionic strengths can have extreme effects upon the activity coefficients for the equilibria under consideration.

A comparison of experimental P_{SO_2} values to P_{SO_2} values calculated at the 90 percent confidence level using equation (20) is given in Table 5.

REFERENCES

1. Miller, L.A. and Terrance, J.D. Process for Recovering Sulfur Dioxide from Gases Containing Same. (Wellman-Lord, Inc., Lakeland, Fla.) U.S. Pat. 3,485,581. 5p., Dec. 23, 1969. 4 refs. (Appl. Nov. 15, 1966, 20 claims).

2. Rosenbaum, J.B. et al. The Citrate Process for Removing SO_2 and Recovering Sulfur from Waste Gases, Proceedings AIME Environmental Quality Conference, Washington, D.C., June 7-9, 1971.

3. Johnstone, H.F. et al. Recovery of Sulfur Dioxide from Waste Gases. Industrial and Engineering Chemistry, 30, 101 - 109, January 1938.

4. Perry, J.H. Chemical Engineers' Handbook (Fourth Edition), Chapter 14, page 11. New York, McGraw-Hill, 1963.

5. Linke, W.F. Solubilities, Inorganic and Metal Organic Compounds. 4th ed. Volume II p. 295, Washington, American Chemical Society, 1958.

Table 5. P_{SO_2} CALCULATED AT 90 PERCENT CONFIDENCE LEVEL--CITRATE SYSTEM

[S(IV)], M	pH	T, °K	Exper. P_{SO_2}	P_{SO_2} Calculated at 90% Confidence Level, mmHg		
				Lower	Expected	Upper
0.0264	3.57	323.	1.35	0.68	1.39	2.83
0.0264	3.65	323.	0.96	0.57	1.15	2.35
0.0264	3.83	323.	0.70	0.37	0.76	1.55
0.0264	4.02	323.	0.45	0.24	0.49	1.00
0.0264	4.11	323.	0.28	0.20	0.40	0.81
0.0264	4.25	323.	0.17	0.14	0.29	0.59
0.0264	3.50	348.	8.84	5.21	10.09	19.55
0.0264	3.69	348.	7.59	3.36	6.52	12.62
0.0264	3.80	348.	4.79	2.61	5.06	9.80
0.0264	4.00	348.	3.89	1.65	3.19	6.18
0.0264	4.10	348.	2.22	1.31	2.53	4.91
0.0264	4.18	348.	1.43	1.09	2.11	4.08
0.0264	4.26	348.	1.01	0.91	1.75	3.40
0.0557	3.65	348.	20.15	7.78	15.08	29.19
0.0557	3.78	348.	16.60	5.77	11.17	21.64
0.0557	3.84	348.	11.50	5.03	9.73	18.85
0.0557	3.92	348.	8.99	4.18	8.09	15.68
0.0557	4.10	348.	7.12	2.76	5.35	10.36
0.0557	4.24	348.	4.92	2.00	3.87	7.50
0.0557	4.33	348.	3.52	1.63	3.15	6.10
0.0557	3.30	303.	1.39	0.48	1.02	2.18
0.0557	3.52	303.	0.98	0.29	0.61	1.31
0.0557	3.65	303.	0.65	0.21	0.46	0.97
0.0557	3.72	303.	0.38	0.18	0.39	0.83
0.0557	3.85	303.	0.27	0.13	0.29	0.61
0.0557	4.00	303.	0.20	0.10	0.20	0.43
0.0557	4.10	303.	0.12	0.08	0.16	0.35

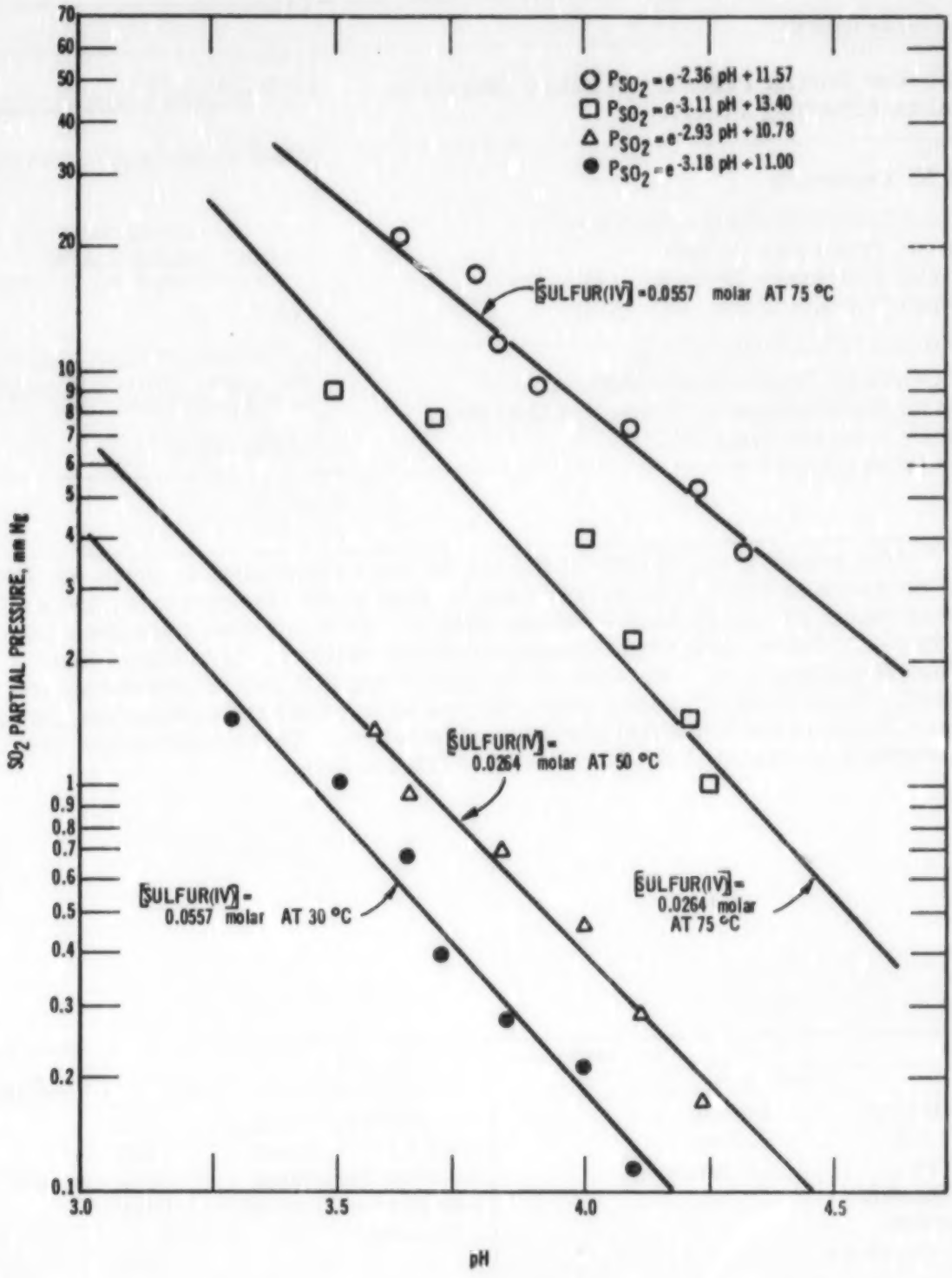

Figure 13. Citrate system equilibrium data.